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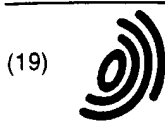
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(54) **Biaxially oriented laminated film**

Biaxial orientierte Verbundfolie

Film multicouche orienté biaxialement

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(56) References cited:  
**EP-A- 0 152 265** **EP-A- 0 158 960**  
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## Description

The present invention relates to a biaxially oriented laminated film, and more particularly to a biaxially oriented laminated film suitable for the base film of magnetic recording media, which gives a high quality image when it is used as the base film of the magnetic recording media and which has an excellent abrasion resistance.

A biaxially oriented polyester film containing practically spherical particles of colloidal silica is known and described in, for example, JP-A-SHO 59-171623. A biaxially oriented laminated polyester film which has an outermost layer containing inorganic particles and which is suitable for a base film of magnetic recording media is also disclosed in, for example, JP-A-HEI 3-1941.

In such conventional biaxially oriented films, however, there is a problem that the surface of the film having fine protrusions is liable to be abraded by rolls and guide pieces used in, for example, a magnetic solution coating process, calendering process, winding process or cassette built-in process, when the film is used as the base film of magnetic recording media and processed into the magnetic recording media. Recently, the speeds of the above processes have increased, so exacerbating the problem.

Further, recently, the dubbing speed of magnetic recording media has been increased by, for example, the development of high-speed magnetic field transfer technology. With the conventional biaxially oriented films described above, when the film is used as the base film of magnetic recording media and the image recorded in the magnetic recording media is dubbed, the signal/noise ratio (S/N) is large and it is difficult to obtain a high-quality image, particularly when the dubbing is carried out at a high speed.

EP-A-0158960 describes an abrasion resistant multilayer biaxially oriented carrier film for recording media comprising a thermoplastic polyester matrix (A) containing finely distributed solid particles to improve the surface roughness, and a cover layer (B) optionally containing fine particles of 0.3-20  $\mu\text{m}$  to compensate for loss of roughness provided by the cover layer (B).

It would be desirable to provide a biaxially oriented laminated film of which the surface is hardly abraded even in high-speed processes (hereinafter, referred to as a film which "excels in abrasion resistance"), and with which a high-quality film of magnetic recording media and the image recorded in the magnetic recording media is regenerated or dubbed, that is, which has a good electromagnetic conversion property (hereinafter, referred to as a film which "excels in electromagnetic conversion property").

A laminated film according to the present invention has at least three layers, at least one of which is biaxially oriented and at least one outermost layer A of which contains particles B, for controlling surface roughness, having a mean primary particle size D1, and additionally contains particles A, as surface protection particles, having a mean primary particle size D which is less than the mean primary particle size D1 of the particles B. The particles A are selected from zirconia, chain-like silica and alumina particles and have a mean primary particle size D in the range of 1 to 100 nm and the particles B are selected from calcium carbonate, crosslinked polymer and colloidal silica particles and have a mean primary particle size D1 in the range of 0.3 to 2  $\mu\text{m}$ . The particles B have a primary particle size distribution with a relative deviation of not greater than 0.6.

The particle density ratio of the particles A at a surface layer is preferably not less than 0.01, and the mean primary particle size D of the particles A and the thickness T of the layer containing the particles A satisfies the equation;  $D \leq T \leq 200D$ .

In the biaxially oriented laminated film according to the present invention, the particles A having a mean primary particle size D appropriately small relative to the thickness T of the outermost layer containing the particles A are efficiently concentrated near the surface of the layer, and the surface can be protected by effect of the particles A. Therefore, the surface of the biaxially oriented laminated film excels in abrasion resistance and is hardly abraded even in high-speed processes. Since the surface of the outermost layer is reinforced, when particles B for forming protrusions for use of the base film of magnetic recording media are contained in the outermost layer, the protrusions formed by the particles B can be hardly abraded because the particles B and the formed protrusions are held by the reinforced surface portions positioned around the particles B. As a result, it becomes easy to form protrusions having a desired size and height on the surface of the film, and when the film is used as the base film of magnetic recording media and the image recorded in the magnetic recording media is dubbed, an excellent electromagnetic conversion property and high-quality image can be obtained.

Next, the present invention will be explained in more detail by embodiments and examples. However, the present invention is not restricted by the embodiments and examples.

In the present invention, the laminated film must have a lamination structure of at least three layers. The number of the layers may be three or more, i.e., may be four, five or more. However, a film of a single layer cannot satisfy good abrasion resistance and electromagnetic conversion property. Further, with a laminated film of two layers it is difficult to satisfy good abrasion resistance and electromagnetic conversion property, particularly difficult to satisfy a good electromagnetic conversion property when the film is used as the base film of magnetic recording media, because, although both surfaces of the magnetic recording media are required to have desired properties, respectively, in most

cases (for example, a property that one surface does not adversely affect the other surface when the film is wound), it is difficult to sufficiently achieve this by a two layer laminated film.

In the laminated film according to the present invention, at least one of the layers constituting the laminated film must be biaxially oriented. Particularly, it is preferable that all the layers constituting the laminated film are biaxially oriented. If all the layers are non-oriented or uniaxially oriented, the film does not have the desired properties.

Although the material of the biaxially oriented laminated film according to the present invention is not particularly restricted, at least one outermost layer containing the particles A is preferably composed of a polyester from the viewpoint of obtaining good formation ability of surface protrusions, abrasion resistance and electromagnetic conversion property. The other layers of the biaxially oriented laminated film are preferably also composed of polyesters from the viewpoint of satisfying good mechanical properties etc.

Although the type of polyester employed for the biaxially oriented laminated film according to the present invention is not particularly restricted, a polyester containing at least one of ethylene terephthalate, ethylene  $\alpha$ ,  $\beta$ -bis(2-chlorophenoxy)ethane-4,4'-dicarboxylate and ethylene 2,6-naphthalate as its main component is preferable. Especially, a polyester whose main component is ethylene terephthalate is particularly preferable. A polyester employed in a film of the present invention may be a blend of two or more kinds of polyester or a copolymerized polymer may be used.

Particles A and B are contained in at least one outermost layer of the biaxially oriented laminated film according to the present invention. Particles A have a relatively small particle size and mainly function to protect the surface of the outermost layer, i.e., the skin of the outermost layer. Particles B have a particle size greater than that of particles A and mainly function to form protrusions on the surface of the outermost layer. The protrusions formed by the particles B improve the running ability at high speed of the film. The surface of the outermost layer reinforced by the particles A can strongly hold the particles B and the formed protrusions, and therefore, the abrasion resistance of the particles B and the formed protrusions can be increased. In addition, the abrasion resistance of the surface itself can be increased by the reinforcement by the particles A.

Since the particles A mainly function to protect the surface of the outermost layer as described above, the particles A contained in the outermost layer are preferably concentrated particularly near the surface layer of the outermost layer. By such a concentration of the particles A, the surface of the film is effectively protected, and the advantage due to the presence of the particles A becomes remarkable. In the present invention, particle density ratio (i.e. ratio of densities of particle distribution) at a surface layer (as later defined) is used as an index which quantitatively indicates to what degree the particles A are concentrated near the surface layer of the outermost layer. The method for determining the particle density ratio at the surface layer is described later. When the particle density ratio at the surface layer is not less than 0.01, the above advantage due to the presence of the particles A becomes remarkable. Therefore, the particle density ratio at a surface layer of particles A in the outermost layer should not be less than 0.01 in the present invention. The particle density ratio at surface layer is more preferably not less than 0.02. When the film is used as the base film of a magnetic recording medium, good electromagnetic conversion property and output property can be obtained by controlling the particle density ratio at surface layer to be not less than 0.01.

In the biaxially oriented laminated film according to the present invention, the relationship between the mean primary particle size D of particles A and the thickness T of the outermost layer containing the particles A must satisfy the following equation.

$$D \leq T \leq 200D$$

If the thickness T is smaller than the particle size D, the force for holding the particles of the outermost layer becomes small and a high abrasion resistance cannot be obtained. If the thickness T is greater than 200D, the advantage for reinforcing the surface of the outermost layer becomes low and the abrasion resistance and the electromagnetic conversion property deteriorate. The abrasion resistance can be increased and an excellent

electromagnetic conversion property can be obtained when the film is used as the base film of magnetic recording media, by controlling the relationship between the mean primary particle size D and the thickness T to the above range. A more preferable range of the mean primary particle size D and the thickness T is  $2D \leq T \leq 100D$ .

The content of particles A is preferably in the range of 0.01 to 2% by weight, and more preferably in the range of 0.02 to 1% by weight. If the content is less than 0.01% by weight, the advantage for reinforcing the surface of the outermost layer expected cannot be obtained because the density of the particles in the layer becomes too low. If the content is greater than 2% by weight, the content is too much and the layer is likely to become brittle.

The particles A are selected from zirconia, chain-like silica and alumina particles. The surface of the outermost layer is effectively reinforced by this selection of the material of the particles A. The mean primary particle size of the particles A is in the range of 1 to 100nm, and preferably in the range of 5 to 100nm. If the mean primary particle size is less than 1nm, the advantage for reinforcing the surface of the outermost layer becomes low.

If the mean primary particle size is greater than 100nm, the particles A themselves form protrusions on the surface and the abrasion resistance is liable to deteriorate.

The particles A are preferably aggregated to some extent from the viewpoint of reinforcement of the surface.

Namely, when the ratio of the mean secondary particle size/the mean primary particle size of the particles A is in the range of 2 to 60, the surface of the outermost layer is effectively reinforced. If the particles A are in a condition of monodispersion or near to that condition, i.e., the ratio of the mean secondary particle size/the mean primary particle size is less than 2, the ability of the particles to reinforce the surface of the outermost layer due to the aggregation of the particles A is reduced.

If the ratio is greater than 60, the aggregated particles become too big and the aggregated particles form brittle protrusions, thereby deteriorating the abrasion resistance.

The particles A can also function as seeds forming non-incorporated particles. Therefore, non-incorporated particles of which seeds are the particles A may be formed in the outermost layer and fine protrusions may be formed on the surface of the layer by the non-incorporated particles.

The mean primary particle size of particles B is in the range of 0.3 to 2  $\mu\text{m}$ , and preferably in the range of 0.3 to 1  $\mu\text{m}$  and a primary particle size distribution with a relative deviation of not greater than 0.6. If the particle size is less than 0.3  $\mu\text{m}$ , the height of the protrusions formed on the surface becomes too small and a good running ability cannot be obtained because the reduction of the friction coefficient of the surface due to the protrusions is small.

If the particle size is greater than 2  $\mu\text{m}$ , the height of the protrusions formed on the surface becomes too large and the abrasion resistance of the surface deteriorates.

When the particles B are contained in at least one outermost layer of the laminated film, the particles B form protrusions on the surface of the outermost layer. In order to form desired protrusions on the surface of the outermost layer by particles B, the mean primary particle size of the particles B and the thickness of the layer containing the particles B should conform to a particular relationship. In the present invention, the relationship between the mean primary particle size D1 of the particles B and the thickness T of the layer containing the particles B is preferably determined so as to satisfy the equation;  $0.5D1 \leq T \leq 5D1$ . The protrusions having uniform and desired height can be formed by the particles B by selecting the particle size D1 and thickness T so as to satisfy the above equation. The electromagnetic conversion property as well as the abrasion resistance of the surface can be further increased by this formation of the uniform and desired protrusions.

The content of the particles B in the outermost layer is preferably in the range of 0.005 to 5% by weight, and more preferably in the range of 0.01 to 1.5% by weight. If the content is less than 0.005% by weight, the degree of roughening of the surface due to the particles B is too low, i.e. the surface is too flat and is likely to be scratched because the friction coefficient of the surface becomes high, and the abrasion resistance deteriorates. If the content is greater than 5% by weight, the content is too high, the outermost layer itself becomes brittle and is liable to be abraded, and the abrasion resistance also deteriorates.

Since the particles B mainly function to form protrusions on the surface of the outermost layer, the distribution of the particle size of the particles B must be appropriately restricted in order to control the height of the formed protrusions as uniform as possible. Namely, the distribution of the particle size of the particles B is preferably a sharp distribution, and the relative standard deviation of the distribution is not greater than 0.6.

The particles B are preferably selected from calcium carbonate particles, crosslinked polymer particles and colloidal silica particles. Protrusions which suffer hardly any abrasion can be efficiently formed on the surface by these specified materials of the particles B. Among these materials, vaterite-type calcium carbonate is high in affinity with polyester etc. because of its high activity. Particularly in a film embodying the present invention, the uniform quality, the uniform particle size and the high affinity with polyester etc. of vaterite-type calcium carbonate particles may be effectively utilized, and protrusions having a desired height and hardly abraded can be formed by the vaterite-type calcium carbonate particles. Crosslinked polymer particles also can be easily formed to have a uniform particle size, and they have a high affinity with the film matrix of polyester etc.

As materials of the crosslinked polymer particles, crosslinked polystyrene and crosslinked divinylbenzene can, for example, be employed.

In the biaxially oriented laminated film according to the present invention, particles C having a mean primary particle size greater than that of the particles A and smaller than that of the particles B may be added in the outermost layer containing the particles A and the particles B. The particles C form protrusions on the surface of the outermost layer which are lower in height than those formed by particles B. The particles C enhance the effect for roughening the surface to decrease the friction coefficient of the surface, and function to further improve the running ability at high speed of the film.

The particles C are preferably selected from colloidal silica particles, crosslinked polymer particles and vaterite-type calcium carbonate particles. Since the particle size of the particles of such materials is relatively easily made uniform, protrusions are formed on the surface such that the protrusions formed by the particles having a uniform particle size supplement the protrusions formed by the particles B. Namely, relatively high protrusions are formed by the particles B, and protrusions are formed by the particles C so as to supplement the protrusions formed by the particles B, i.e., so as to be positioned between the protrusions formed by the particles B or on the protrusions formed by the particles B. As a result, the surface is roughened more uniformly without forming too big protrusions, the friction

coefficient of the surface is greatly decreased and an excellent running ability can be obtained. Moreover, since the particles C of such materials have a high affinity with the film matrix of polyester etc., the particles C also can reinforce the protrusions formed by the particles B.

The mean primary particle size of particles C is preferably in the range of 0.05 to 1.5  $\mu\text{m}$ , and more preferably in the range of 0.1 to 1  $\mu\text{m}$ . If the particle size is less than 0.05  $\mu\text{m}$ , the height of the protrusions formed on the surface becomes too small and the advantage for improving the running ability is small. If the particle size is greater than 1.5  $\mu\text{m}$ , some of the protrusions formed by the particles C are higher than the protrusions formed by the particles B and the abrasion resistance of the surface may deteriorate.

The content of the particles C in the outermost layer is preferably in the range of 0.005 to 2% by weight, and more preferably in the range of 0.01 to 1.5% by weight. If the content is less than 0.005% by weight, the advantage of improving the running ability cannot be expected because the number of the protrusions formed by the particles C is too small. If the content is greater than 2% by weight, the number of the particles is too great, the outermost layer itself becomes brittle and the particles are likely to drop out.

Since the particles C mainly function to enhance roughening of the surface by forming relatively small protrusions without damaging the formation of the protrusions by particles B, the particle size of the particles C is desirably as uniform as possible, that is, it is desired that there are no protrusions which are too big. For this, the distribution of the particle size of the particles C is preferably restricted appropriately. Namely, the distribution of the particle size of the particles C is preferably a sharp distribution, and the relative standard deviation of the distribution is preferably not greater than 0.6.

In the laminated film according to the present invention, the relative standard deviation of height distribution of protrusions on at least one surface of the film is preferably not greater than 1.2, and more preferably not greater than 1.1. If the relative standard deviation is greater than the above value, undesired protrusions which are too big are intermixed between desired protrusions, and the electromagnetic conversion property as well as the abrasion resistance may deteriorate.

Further, in the biaxially oriented laminated film according to the present invention, the surface resistivity of at least one outermost layer of the laminated film is preferably not greater than  $1 \times 10^{14} \Omega/\square$ , more preferably not greater than  $1 \times 10^{13} \Omega/\square$ , and further more preferably not greater than  $1 \times 10^9 \Omega/\square$ . If the surface resistivity is within the above range, the electro static charge during running is suppressed so as to be small, the running ability of the film is further increased, and shaking of regenerated images can be prevented when the laminated film is used as the base film of magnetic recording media.

In order to satisfy the above surface resistivity, at least one outermost layer of the laminated film preferably contains sulphate represented by the chemical formula  $[\text{C}_n\text{H}_{2n+1}-\text{C}_6\text{H}_4-\text{SO}_3\text{M}]$  ( $n=6-30$ ,  $\text{M}=\text{Na}, \text{Li}$ ). "n" is preferably in the range of 9 to 18. M is preferably Na.  $[-\text{C}_6\text{H}_4-]$  is benzene ring, and the position of  $[\text{SO}_3\text{M}]$  on the benzene ring is preferably the para position although the ortho or meta position is available. The content of sulphate is preferably in the range of 0.2 to 5% by weight from the viewpoint of increase of abrasion resistance and electromagnetic conversion property, and more preferably in the range of 0.5 to 2% by weight.

Further, in the biaxially oriented laminated film according to the present invention, the outermost layer may contain polyalkylene glycol from the viewpoint of increase of abrasion resistance and electromagnetic conversion property. Polyethylene glycol is preferable as the polyalkylene glycol. The molecular weight of polyalkylene glycol is preferably in the range of 100 to 10000, and more preferably in the range of 500 to 5000. The content of polyalkylene glycol is preferably in the range of 0.2 to 5% by weight from the viewpoint of increase of abrasion resistance and electromagnetic conversion property, and more preferably in the range of 0.5 to 2% by weight.

The intrinsic viscosity (IV) of the polymer of the outermost layer of the laminated film according to the present invention is preferably in the range of 0.4 to 0.9 because the abrasion resistance is further increased.

In the laminated film according to the present invention, other polymers may be blended as long as the desired properties are not unduly adversely affected. Further, a generally used additive, for example, oxidation inhibitor, thermal stabilizer, lubricant, ultraviolet absorbent etc., may be added at a volume which does not substantially decrease the advantages according to the present invention.

In the laminated film according to the present invention, parameter P10 of the surface roughness of at least one outermost layer is preferably not greater than 250nm. If the parameter P10 is greater than this value, the abrasion resistance is likely to be decreased and the electromagnetic conversion property is likely to be decreased. More preferably, the parameter P10 is not greater than 200nm.

In a case where the laminated film according to the present invention has four or more layers, the laminated film can have a lamination structure of, for example, an outermost layer A containing particles A/a cover layer B/an intermediate layer C/another layer D, or layer A/layer B/layer C/layer B/layer D. The thickness of the cover layer B may be appropriately set within the range of not less than 0.2  $\mu\text{m}$  depending upon the condition of the intermediate layer C. Namely, since the layer B functions as a smoothing layer against the layer C for the layer A, the thickness of the layer B can be set depending upon its desired use as long as the smoothness effect can be obtained. For example, the

thickness can be set appropriately large for use in a floppy disk etc., and appropriately small for use in a magnetic tape etc. However, if the thickness is less than 0.2  $\mu\text{m}$ , the advantage to be expected may not be obtained.

Although it is not necessary that the layer B contains particles, it is preferred that the layer B contains particles in an amount of up to 2% inclusive by weight because the layer B itself can be reinforced by the particles contained. In

such a case, the kind of particles present may be the same as or different from that of the particles present in the layer A. The intermediate layer C substantially constitutes a center layer of a biaxially oriented laminated film embodying the present invention. The thickness of the layer C may be appropriately set within the range of not less than 0.1  $\mu\text{m}$ . For example, since both surfaces of the layer C are covered with layers B and the layer B functions as a smoothing layer for the layer A, the layer C may have a mechanical strength etc., at an appropriate level. Therefore, recycle polymer may be contained in this layer C.

The "recycle polymer" may be, for example, with respect to a polyester film, a polymer of which end carboxylic acid of polyester is not less than 55 equivalents/ $10^6$  g and haze in the polymer is not greater than 18%.

Next, a process for producing the biaxially oriented laminated film according to the present invention will be explained. However, the process is not particularly restricted to the following.

As the method for incorporating particles in polyester, for example, a method for dispersing the particles in ethylene glycol, which is the diol component of the polyester, in the form of a slurry, and thereafter copolymerizing the ethylene glycol with a dicarboxylic acid component, is preferable. When the particles are added, for example, the particles can be dispersed very well by adding the particles in the form of water sol or alcohol sol formed when copolymerized, as they are, i.e., without drying. By such a method for adding the particles, good abrasion resistance and electromagnetic conversion property can be obtained. Alternatively, a method for blending the water sol of the particles directly with polyester pellets and mixing the particles with the polyester by supplying the blended water sol and the polyester pellets to a twin-screw extruder is also very effective to obtain the desired advantages. As the method for controlling the content of the particles, a method for making master pellets having a high concentration by the above method and diluting the master pellets with polyester which substantially does not contain particles when the film is produced is effective.

Next, a laminated polyester film having three or more layers is produced using the above polyester pellets. The polyester pellets prepared by the above method are blended with other pellets at a predetermined rate, and the blended pellets are supplied to a known extruding apparatus for melting and lamination after the pellets are dried. The molten polymer is delivered out from a die in the form of a sheet, and the sheet is cooled and solidified on a casting roll to form a non-stretched film. Namely, the lamination is carried out by using two or more extruders and a die having a composite manifold or a feed block for three or more layers (for example, a feed block having a rectangular shaped lamination portion), a molten sheet having three or more layers is delivered out from a die, and the delivered sheet is cooled on a casting roll to form a non-stretched film. In such a manner, it is effective to install a static mixer and a gear pump in the polymer path. Further, it is effective to set the temperature of the extruder for extruding the polymer constituting the outermost layer to a temperature lower by 5 to 10°C than the temperature of the extruder for extruding the polymer constituting the inner layers.

Next, the non-stretched film obtained is biaxially stretched and biaxially oriented. As the stretching process, a sequential biaxial stretching or a simultaneous biaxial stretching can be employed. Especially, a process for using a sequential biaxial stretching wherein firstly longitudinal stretching and secondly transverse stretching are carried out, dividing the longitudinal stretching into three or more stages and setting the total draw ratio of the longitudinal stretching to 3.0 to 6.5 times is particularly preferable. Although it is difficult to determine the optimum temperature for the longitudinal stretching to a particular temperature because the optimum temperature varies depending on the kind of polyester, usually setting the temperature of the first stage to 50 to 130 °C and the temperatures of other stages after the first stage to a higher temperature is effective. The stretching rate in the longitudinal direction is preferably in the range of 5000 to 50000%/min. The transverse stretching is usually conducted by using a stenter. The stretching rate in the transverse direction is preferably in the range of 1000 to 20000%/min, and the temperature for the stretching is preferably in the range of 80 to 160°C. The biaxially stretched film thus formed is then heat treated. The temperature of the heat treatment is preferably in the range of 170 to 220 °C, more preferably in the range of 180 to 200°C, and the time of the heat treatment is preferably in the range of 0.2 to 20 seconds.

Next, methods for determining the characteristics in the present invention and estimating the effects according to the present invention will be explained.

#### (1) Mean primary particle size of particles:

The film containing particles is cut in its thickness direction to make a very thin piece having a thickness of 1000 to 8000 Å, and the piece is observed by using a transmission type electron microscope (for example, JEM-1200EX produced by Nippon Denshi Corporation). When the piece is observed at a magnification of about 100,000 times, a minimum particle size (a primary particle size), into which the observed particles cannot be further divided, can be

observed. This observation is carried out on 100 fields of view, and the mean value is defined as the mean primary particle size of the particles. Alternatively, the specific surface area of the particles is determined by using BET adsorption isotherm, the particle size is determined from the determined specific surface area by using the following equation when the shape of the particles is assumed to be spherical, and the determined particle size may be defined as the mean primary particle size of the particles. Particle size =  $6 / (\text{Density of particle} \times \text{Specific surface area})$

(2) Secondary particle size of particles:

Particles are dispersed in ethylene glycol or water to make a slurry, the particle size distribution of the slurry is determined by using a decanter type particle size measuring apparatus, and the mean particle size determined from the determined particle size distribution is defined as the secondary particle size of the particles. Alternatively, the equivalent diameter of the particles is determined from the above (1), and the mean equivalent diameter may be defined as the secondary particle size of the particles.

(3) Relative standard deviation of distribution of particle size of particles B:

The primary particle sizes of 1000 particles B are determined in the manner described in the above (1), and the relative standard deviation of the distribution of particle size is determined by the following equation. Relative standard deviation of distribution of particle size = Standard deviation / mean particle size

(4) Particle density ratio at surface layer:

The ratio of the density of the element originating from the particles contained in the film to the density of the carbon in the polyester determined by using secondary ion mass spectrum (SIMS) is defined as the particle density, and the analysis is carried out along the direction of thickness of the film. The ratio A/B of the particle density A at the outermost point (at a depth of 3nm) measured by SIMS to the particle density B at a depth of 30nm measured by continuing the SIMS analysis along the direction of thickness of the film is defined as the particle density ratio at surface layer. In this determination, if impurities are contained in the film, the density ratio with the elements of the impurities is sometimes detected together with the above analysis. However, this density ratio originating from the impurities should be neglected on the analysis. The measuring apparatus and the measuring conditions are as follows:

① Measuring apparatus:

Secondary ion mass spectrum analysis apparatus;  
A-DIDA3000 produced by ATOMIKA (Germany)

② Measuring conditions:

Primary ion species;  $O_2^+$   
Primary ion acceleration voltage; 12KV  
Primary ionic current; 75nA  
Raster area;  $800\mu m^2$   
Analysis area; gate 100%  
Degree of vacuum for measurement;  $1 \times 10^{-8}$  Torr  
E-GUN; 0.5KV-3.0KV

(5) Content of particles:

The film is treated with a solvent which dissolves the polyester but which does not dissolve the particles, and the particles are separated from the polyester by centrifugation. The content of the particles is defined as the ratio of the weight of the separated particles to the total weight of the film (% by weight). Alternatively, as needed, the determination may be carried out by utilizing thermal decomposition, infrared spectrophotometry, fluorescent X-ray diffraction, Raman scattering or SEM-XMA.

The contents of the particles of the laminated layer and the base layer can be distinguished from each other by cutting off the laminated layer. Furthermore, if necessary, the content may be determined by calculating the number of the particles in each section observed by using TEM.



## (6) Relative standard deviation of height distribution of protrusions:

The signal of the data of the height of the protrusions measured by using a two beam and two detector type scanning electron microscope (ESM-3200; produced by Elionics Corporation) and a cross section measuring apparatus (PMS-1; produced by Elionics Corporation) and by scanning with such apparatus under conditions such that the height of the flat portion of the surface of the film is set as zero is sent to an image processor (iBAS-2000; produced by Elionics Corporation), and the image of the protrusions of the film surface is reconstructed on the display of the image processor. Then, the highest value among the heights of the projected portions of each protrusion, which are determined by placing the protrusion in the image of the image processor in a binary condition, is defined as the height of the protrusion. This measurement is repeated 500 times changing the area to be observed, and the mean height thereof and the standard deviation thereof are determined.

The magnification of the scanning electron microscope is selected from the range of 1000 to 8000 times. The relative standard deviation of height distribution of the protrusions is determined by the following equation.

$$\text{Relative standard deviation} = \text{standard deviation} / \text{mean height}$$

## (7) Surface resistivity of film:

The film to be determined is placed on a relatively thick rubber sheet so that the surface to be measured is at the upper side. A pair of rectangular electrodes of brass having a length equal to the length of a side of a square and a width of 1/10 of the length, whose bottom surfaces are polished, are placed on the film such that the electrodes are positioned just at the sides of the square opposite to each other. While a pressure of 0.2 kg/cm<sup>2</sup> is applied on the electrodes, the electrical resistivity between the electrodes is measured as the surface resistivity of the film. In this measurement, the size of the electrodes may be appropriately selected depending upon the film to be determined. The unit of the surface resistivity is  $\Omega/\square$ .

## (8) Identification and Content of sulphate:

The composition and the content of the sulphate contained in the laminated layer is determined by ashing treatment or infrared absorption spectrum.

## (9) Identification and content of polyalkylene glycol:

The composition and the content of the polyalkylene glycol contained in the laminated layer is determined by thermal decomposition treatment and mass spectrum or infrared absorption spectrum.

## (10) Thickness of layer:

The ratio of the density of the element originating from the particles contained at the highest density in the film to the density of the carbon in the polyester ( $M + ^{12}C + ^{16}O$ ) determined by using secondary ion mass spectrum (SIMS) is defined as the particle density, and the analysis is carried out along the direction of thickness of the outermost layer. The particle density in the outermost layer increases as distanced from the surface because the surface constitutes a boundary surface. In the film according to the present invention, the particle density becomes the maximum at a depth [I] and thereafter decreases again. Based on this particle density curve, a depth [II], at which the particle density becomes half of the maximum value, is defined as the thickness of the outermost layer (where, [II] > [I]). In a case where the particles contained at the highest density in the film are organic particles, because the determination by SIMS is difficult, the thickness of the outermost layer may be determined by measuring the depth profile of the particle density by X-ray photoelectron spectrum (XPS), infrared spectroscopic analysis (IR) or a confocal microscope while etching from the surface, and determining in a manner similar to the above-described manner. Further, the thickness may be determined by observing the cross section of the film or using a level difference measuring apparatus for thin membranes.

## (11) Parameter of surface roughness P10:

Using a photo-interference type three-dimensional surface analysis apparatus (TOPO-3D; produced by WYKO Corporation, objective lens; 40-200 times, use of a high resolution camera is effective), the image of the protrusions of the film surface is constructed on the display of an image processor. The mean value of ten points from the highest protrusion in the constructed image is defined as P10. The measurement is repeated twenty times and the mean value

thereof is defined as the parameter of surface roughness P10 (unit: nm).

(12) Intrinsic viscosity of polymer (IV):

5 The intrinsic viscosity of polymer is determined using o-chlorophenol as the solvent.

(13) Haze:

10 Polyester 100mg is dissolved in mixture solvent 10ml of phenol/tetrachloromethanol (6/4 ratio by weight) and the haze of the polymer solution is measured by ASTM-D-1003-52.

(14) Quantity of carboxyl end group:

In accordance with the method of Maurice.

15 Polymer 2g is dissolved in mixture solvent 50ml of o-cresol/chloroform (7/3 ratio by weight) and the carboxyl end group is titrated by N/20-NaOH methanol solution. Quantity of carboxyl end group is expressed as equivalent/polyester 10<sup>6</sup> g.

(15) Shaking of regenerated image when the film is used as a base film of a magnetic recording medium:

20 A magnetic coating solution is coated with a gravure roll on the surface of the film so that the thickness after drying is 3  $\mu$ m. The composition of the magnetic coating solution is as follows.

(Composition of magnetic coating solution)(All parts are by weight.)

25 **Co-containing iron oxide: 100 parts**

**Vinyl chloride/vinyl acetate copolymer: 10 parts**

**Polyurethane elastomer : 10 parts**

30 **Polyisocyanate : 5 parts**

**Lecithin : 1 parts**

35 **Methylethylketone : 75 parts**

**Methylisobutylketone : 75 parts**

40 **Toluene : 75 parts**

**Carbon black : 2 parts**

45 **Lauric acid : 1.5 parts**

After the above composition is blended and dispersed for 48 hours by a ball mill, a curing agent is added (6 parts). The mixture obtained is filtered to prepare the magnetic coating solution. The magnetic coating solution is coated on the film and the coated magnetic layer is magnetically oriented and dried at 110°C.

50 After calendering the film by a small test calendering machine (steel roll/nylon roll; 5 stages) at a temperature of 70°C and a pressure of 200 kg/cm, the film is wound in the form of a roll. The film roll is cured at 50°C for 48 hours, and thereafter, the film is slit to make a magnetic tape having a width of 1/2 inch.

55 The magnetic tape thus obtained is incorporated into a VTR cassette, and using a domestic video tape recorder, an image of vertical lines is recorded in an atmosphere of 40 °C and 80%RH. The image recorded in the tape is regenerated in the same atmosphere using the VTR. The degree of shaking of the regenerated image of vertical lines after 60 minutes from the start of the regeneration is estimated by observation. If there is no shaking, the shaking of the regenerated image is assessed as good, and if the shaking can be recognized, the shaking of regenerated image is assessed as good.

## (16) Electromagnetic conversion property:

100% chromatic signal generated by a television testing wave generator is recorded in the tape described in the above (15) using a domestic VTR, and chromatic S/N is determined from the regenerated signal using a color video noise measuring apparatus (unit: dB).

## (17) Abrasion resistance:

The film is slit into a tape having a width of 1/2 inch. The tape is run by 200m under conditions such that a safety razor is pressed onto the tape so that the knife edge is positioned lower by 0.5mm than the level of the tape applied with a tension (running speed: 200 m/min, tension: 100g). The height of the powder on the razor, which is cut off from the tape by the razor and adhered to the razor, is determined by a microscope, and the height is defined as the abraded amount ( $\mu\text{m}$ ). If the abraded amount is not greater than 180 $\mu\text{m}$ , the abrasion resistance is good, and if the abraded amount is greater than 180  $\mu\text{m}$ , the abrasion resistance is not good.

## (18) Tracking resistance:

A signal is recorded in a floppy disk under conditions of (a) a temperature of 25°C and a relative humidity of 20%, and (b) a temperature maintained at 25°C and a relative humidity of 70%. The output envelopes under the condition of 25 °C and 20%RH and under the condition of 25°C and 70%RH are compared. The smaller the difference between both output envelopes, the more excellent is the tracking resistance. If the difference is greater than 3dB, the tracking resistance is assessed as good, and if the difference is not greater than 3dB, the tracking resistance is assessed as excellent.

## (19) Durability:

The same track recorded in the floppy disk in the same manner as that of the above (16) is scanned at a running speed of 6 m/sec not less than 1000,000 times, and thereafter, the output envelope is determined. If scratches are recognized on the magnetic surface and the output envelope is unstable, the durability is assessed as good. If no scratches are recognized on the magnetic surface and the output envelope is stable, the durability is assessed as excellent.

Preferred examples will be hereinafter explained together with comparative examples.

Example 1 (Table 1)

Zirconia particles having a mean primary particle size of 20nm prepared as particles A were dispersed in ethylene glycol using glass beads having a diameter of 50  $\mu\text{m}$  as medium. After removing the glass beads, the mixture was polymerized with terephthalic acid to make master pellets of polyethylene terephthalate.

On the other hand, vaterite-type calcium carbonate particles having a mean primary particle size of 0.8 $\mu\text{m}$  prepared as particles B were dispersed uniformly in ethylene glycol using the above media dispersion method, and master pellets containing particles B were prepared in a manner similar to that described above.

The above master pellets containing particles A, the master pellets containing particles B and pellets of polyethylene terephthalate which did not contain particles were blended such that the contents of particles A and particles B were 0.3 wt% and 0.4 wt%, respectively. The blended pellets were supplied to a vent-type twin-screw extruder and melted at a temperature of 280 °C (polymer I). Further, another extruder was prepared, the pellets with no particles were dried at a temperature of 180 °C for 8 hours (3 Torr), the dried pellets were supplied to the extruder and melted at a temperature of 290 °C (polymer II). After filtering these two polymers at a high accuracy in filtration degree, the polymers were laminated by a feed block for three layers having a rectangular shaped lamination portion so that the polymer II was positioned as the base layer and the polymer I was laminated on both surfaces of the base layer as both outermost layers. The laminated polymer was delivered out from a fish tail type die in the form of a sheet, the delivered sheet was cast on a casting drum of which surface temperature was controlled at 30°C and cooled and solidified on the drum using an electrostatic charging method to form a non-stretched film having a thickness of about 160 $\mu\text{m}$ . In this casting, the draft ratio was 6.5.

The non-stretched film obtained was stretched in the longitudinal direction at three stages the respective conditions of temperatures and draw ratios of which were 123 °C, 1.2 times; 126°C, 1.45 times; and 114 °C, 2.3 times. The uniaxially stretched film obtained was stretched, using a stenter, in the transverse direction at two stages the respective conditions of temperatures and draw ratios of which were 111°C, 3.7 times and 113 °C, 1.2 times, and heat treated at conditions of a temperature of 200 °C and a constant length for five seconds to make a biaxially oriented film having

a thickness of 13  $\mu\text{m}$ . The thickness T of the outermost layer was 1.0  $\mu\text{m}$  and the relationship between the thickness T and the particle size D of particles A was  $T=50D$ . The particle densities of particles A and the lamination thicknesses of both outermost layers were the same, and the particle density ratio at surface layer was 0.06.

The electromagnetic conversion property of the film was 2.6dB in chromatic S/N. The abrasion resistance was 55  $\mu\text{m}$  and it was good. Thus, in a case where the kind, the particle size, the content, the particle density ratio at surface layer and the relationship between the thickness T and the particle size D in the outermost layer satisfied the preferred requirements of the present invention, a film having an excellent electromagnetic conversion property and a good abrasion resistance was obtained.

Examples 2-4, Comparative Examples 1-4 (Table 1)

Biaxially oriented laminated films were made in a manner similar to that of Example 1, changing the kind, the particle size, the content, the particle density ratio at surface layer and the relationship between the thickness T and the particle size D in the outermost layer. If any condition was out of the range required by the present invention, an excellent electromagnetic conversion property and a good abrasion resistance was not simultaneously achieved.

TABLE 1

	Particle A				Particle B				Thickness of outermost layer ( $\mu\text{m}$ )	Electro-magnetic conversion property (dB)	Abrasion resistance ( $\mu\text{m}$ )
	Kind	Primary particle size ( $\mu\text{m}$ )	Secondary/Primary particle size	Content (wt%)	Particle density ratio at surface layer	Kind	Primary particle size ( $\mu\text{m}$ )	Content (wt%)			
Example 1	zirconia	2.0	1.0	0.3	0.006	vaterite-type calcium carbonate	0.8	0.4	1.0	+2.6	5.5
Example 2	alumina	1.0	2.0	0.5	0.07	Crosslinked polymer particle	0.6	0.3	1.2	+2.8	7.5
Example 3	silica	4.0	8	0.2	0.03	vaterite-type calcium carbonate	0.4	0.5	0.7	+2.4	8.0
Example 4	silica	4.0	4	0.5	0.03	Crosslinked polymer particle	0.5	0.2	0.7	+2.2	6.0
Comparative Example 1	—	—	—	—	—	vaterite-type calcium carbonate	0.6	0.5	5.0	0	3.50
Comparative Example 2	zirconia	2.0	1.0	0.3	0.06	—	—	—	5.0	+0.5	2.50
Comparative Example 3	zirconia	4.0	6	0.5	0.005	silica	0.6	0.4	5.0	-0.5	3.00
Comparative Example 4	silica	1.50	1	0.1	0.002	vaterite-type calcium carbonate	0.5	0.002	3.0	-0.4	4.00

Example 5 (Table 2)

Zirconia particles having a mean primary particle size of 20nm prepared as particles A were dispersed in ethylene glycol using glass beads having a diameter of 50  $\mu\text{m}$  as medium. After removing the glass beads, the mixture was polymerized with terephthalic acid to make master pellets of polyethylene terephthalate.

On the other hand, calcium carbonate particles having a mean primary particle size of 0.8 $\mu\text{m}$  prepared as particles B were dispersed uniformly in ethylene glycol using the above media dispersion method, and master pellets containing particles B were prepared in a manner similar to that described above.

Further, colloidal silica particles having a mean primary particle size of 0.4  $\mu\text{m}$  prepared as particles C were dispersed uniformly in ethylene glycol using the above media dispersion method, and master pellets containing particles C were prepared in a manner similar to that described above.

The above master pellets containing particles A, the master pellets containing particles B, the master pellets containing particles C and pellets of polyethylene terephthalate which did not contain particles were blended such that the contents of particles B and particles C were 0.4 wt% and 0.1 wt%, respectively. The blended pellets were supplied to a vent-type twin-screw extruder and molten at a temperature of 280°C (polymer I). Further, another extruder was prepared, the pellets with no particles were dried at a temperature of 180 °C for 8 hours (3 Torr), the dried pellets were supplied to the extruder and molten at a temperature of 290 °C (polymer II). After filtering these two polymers at a fine mesh filtration degree, the polymers were laminated by a feed block for three layers having a rectangular shaped lamination portion so that the polymer II was positioned as the base layer and the polymer I was laminated on both surfaces of the base layer as both outermost layers. The laminated polymer was delivered out from a fish tail type die in the form of a sheet, the delivered sheet was cast on a casting drum of which surface temperature was controlled at 30°C and cooled and solidified on the drum using an electrostatic charging method to form a non-stretched film having a thickness of about 160 $\mu\text{m}$ . In this casting, the draft ratio was 6.5.

The non-stretched film obtained was stretched in the longitudinal direction at three stages the respective conditions of temperatures and draw ratios of which were 123 °C, 1.2 times; 126°C, 1.45 times; and 114 °C, 2.3 times. The uniaxially stretched film obtained was stretched, using a stenter, in the transverse direction at two stages the respective conditions of temperatures and draw ratios of which were 111°C, 3.7 times and 113 °C, 1.2 times, and heat treated at conditions of a temperature of 200 °C and a constant length for five seconds to make a biaxially oriented film having a thickness of 13  $\mu\text{m}$ . The thickness T of the outermost layer was 1.0 $\mu\text{m}$  and the relationship between the thickness T and the particle size D of particles A was  $T=50D$ .

The electromagnetic conversion property of the film was 2.3dB in chromatic S/N. The abrasion resistance was 35 $\mu\text{m}$  and it was good. Thus, in a case where the kind, the particle size, the content and the relationship between the thickness T and the particle size D in the outermost layer satisfied the preferred requirements of the present invention, a film having an excellent electromagnetic conversion property and a good abrasion resistance was obtained.

Examples 6-8, Comparative Examples 5-8 (Table 2)

Biaxially oriented laminated films were made in a manner similar to that of Example 5, changing the kind, the particle size, the content and the relationship between the thickness T and the particle size D in the outermost layer. If any condition was out of the range required by the present invention, an excellent electromagnetic conversion property and a good abrasion resistance were not simultaneously achieved.

TABLE 2

	Particle A			Particle B (Calcium carbonate)		Particle C				Thickness of outermost layer ( $\mu$ m)	Electro- magnetic conversion property (dB)	Abrasion resistance ( $\mu$ m)
	Kind	Primary particle size (nm)	Secondary/ Primary particle size	Particle size ( $\mu$ m)	Content (wt%)	Kind	Particle size ( $\mu$ m)	Content (wt%)	Relative standard deviation of distribution of particle size			
Example 5	zirconia	20	7	0.8	0.4	Colloidal silica	0.4	0.1	0.5	1.0	+2.3	3.5
Example 6	chain- like silica	20	10	0.6	0.4	Colloidal silica	0.5	0.2	0.3	1.5	+2.5	7.0
Example 7	alumina	10	10	0.5	0.3	Crosslinked polymer particle	0.6	0.2	0.5	0.7	+2.8	8.0
Example 8	zirconia	40	5	0.5	0.5	vaterite- type calcium carbonate	0.5	0.3	0.3	1.0	+2.1	6.5
Comparative Example 5	—	—	—	0.6	0.4	Colloidal silica	0.4	0.1	0.5	3.0	0	2.50
Comparative Example 6	alumina	10	10	—	—	Colloidal silica	0.4	0.1	0.5	3.0	-0.2	3.20
Comparative Example 7	alumina	10	20	0.6	0.4	—	—	—	—	5.0	-0.4	2.80
Comparative Example 8	zirconia	20	10	0.6	3.0	vaterite- type calcium carbonate	0.8	0.002	1.0	5.0	+0.2	2.40

Example 9 (Table 3)

Chain-like silica particles having a mean primary particle size of 10nm and calcium carbonate particles were dispersed in ethylene glycol using glass beads having a diameter of 50  $\mu\text{m}$  as medium. After removing the glass beads, the mixture was polymerized with terephthalic acid to make master pellets of polyethylene terephthalate. The content of the particles in the polyester was 1.0% by weight.

The above master pellets (30 parts by weight) containing the particles and pellets of polyethylene terephthalate with no particles (70 parts by weight) were blended, and the blended pellets were supplied to a vent-type twin-screw extruder 1 and melted at a temperature of 280°C (polymer I).

Further, another extruder 2 was prepared, after the master pellets (10 parts by weight) containing the particles and pellets of polyethylene terephthalate with no particles (90 parts by weight) were blended, the blended pellets were dried at a temperature of 180 °C for 8 hours (3 Torr), and the dried pellets were supplied to the extruder and melted at a temperature of 290 °C (polymer II). Furthermore, another extruder 3 was prepared, after recycle chip (30 parts by weight) and pellets of polyethylene terephthalate with no particles (70 parts by weight) were blended, the blended pellets were dried at a temperature of 180 °C for 8 hours (3 Torr), and the dried pellets were supplied to the extruder and melted at a temperature of 290 °C (polymer III). After filtering these three polymers at a fine mesh filtration degree, the polymers were laminated by a feed block for five layers having a rectangular shaped lamination portion so that the polymer III was positioned as the center layer, the polymer II was laminated on both surfaces of the center layer as cover layers and the polymer I was laminated on the surfaces of both cover layers as the outermost layers. The laminated polymer was delivered out from a fish tail type die in the form of a sheet, the delivered sheet was cast on a casting drum of which surface temperature was controlled at 30 °C and cooled and solidified on the drum using an electrostatic charging method to form a non-stretched film having a thickness of about 160 $\mu\text{m}$ . In this casting, the draft ratio was 6.5.

The non-stretched film obtained was stretched in the longitudinal direction at three stages the respective conditions of temperatures and draw ratios of which were 123 °C, 1.2 times; 126°C, 1.45 times; and 114 °C, 2.3 times. The uniaxially stretched film obtained was stretched, using a stenter, in the transverse direction at two stages the respective conditions of temperatures and draw ratios of which were 111°C, 3.7 times and 113 °C, 1.2 times, and heat treated at conditions of a temperature of 200 °C and a constant length for five seconds to make a biaxially oriented film having a thickness of 15 $\mu\text{m}$ . The thickness T of the outermost layer was 1.0 $\mu\text{m}$  and the relationship T/D between the thickness T and the particle size D of the particles was 100. The particle densities of the particles and the lamination thicknesses of both outermost layers were the same. The intrinsic viscosity (IV) of the polymer of the outermost layers was 0.615. The parameter of surface roughness P10 of this film was 100nm.

The electromagnetic conversion property of the film was 2.0dB in chromatic S/N. The abrasion resistance was 90 $\mu\text{m}$  and it was good. Thus, in a case where the particle size, the content of the particles and the thickness of each layer satisfied the preferred requirements of the present invention, a film having an excellent electromagnetic conversion property and a good abrasion resistance was obtained.

Examples 10-12, Comparative Examples 9-14 (Table 3)

Biaxially oriented laminated films were made in a manner similar to that of Example 9, changing the particle size, the content of the particles and the thickness of each layer. If any condition was out of the range required by the present invention, an excellent electromagnetic conversion property and a good abrasion resistance were not simultaneously achieved.



TABLE 3

	Layer A			Layer B		Layer C		Parameter of surface roughness P10 (nm)	Relative standard deviation of height distribution of protrusions	Electromagnetic conversion property (dB)	Abrasion resistance ( $\mu\text{m}$ )	Lamination structure
	Thickness ( $\mu\text{m}$ )	Thickness/particle size	Content (wt%)	Thickness ( $\mu\text{m}$ )	Content (wt%)	Thickness ( $\mu\text{m}$ )	Recycle chip					
Example 9	1.0	100	0.3	2.0	0.1	9.0	○	100	0.5	+2.0	90	A/B/C/B/A (five layers)
Example 10	1.5	150	0.5	1.0	0	10.0	○	150	0.6	+1.7	110	A/B/C/B/A (five layers)
Example 11	0.8	80	0.3	4.0	0.1	5.4	○	120	0.6	+1.8	85	A/B/C/B (four layers)
Example 12	1.0	100	0.2	3.0	0.2	7.0	○	125	1.0	+1.2	120	A/B/C/B/A (five layers)
Comparative Example 9	15	1500	0.2	—	—	—	—	320	1.1	0	250	single layer
Comparative Example 10	5.0	500	0.3	10.0	0.4	—	—	190	1.2	+0.2	220	A/B (two layers)
Comparative Example 11	5.0	500	0.5	9.0	0.2	—	—	280	1.0	+0.3	300	A/B/A (three layers)
Comparative Example 12	3.0	300	0.2	10.0	0	3.0	×	200	1.2	+0.5	190	A/B/C (three layers)
Comparative Example 13	0.8	no chain-like silica	4.0		5.0	3.0	×	250	1.1	+1.0	350	A/B/C/B (four layers)
Comparative Example 14	1.0	no chain-like silica	0.1		3.0	12.0	○	300	1.2	+0.2	190	A/B/C/B/A (five layers)

Examples 13 and 14, Comparative Example 15 (Table 4)

Biaxially oriented laminated films having relatively large thicknesses were made as base films of floppy disks in a manner similar to that of Example 9. A great smoothing effect could be obtained by layers B having a relatively large thickness, and a large amount of recycle chips could be contained in layer C having a large thickness. As shown in Table 4, in a case where each property is in a preferred range embodying the present invention, excellent tracking resistance and durability can be obtained, and it is understood such biaxially oriented laminated films embodying the present invention is an excellent film as a base material of a floppy disk.

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TABLE 4

	Layer A			Layer B		Layer C		Parameter of surface roughness P10 (nm)	Relative standard deviation of height distribution of protrusions	Tracking resistance	Durability	Lamination structure
	Thickness ( $\mu\text{m}$ )	Thickness/particle size	Content (wt%)	Thickness ( $\mu\text{m}$ )	Content (wt%)	Thickness ( $\mu\text{m}$ )	Recycle chip					
Example 13	1.0	100	0.3	10.0	0.1	53.0	O	100	0.5	excellent	excellent	A/B/C/B/A (five layers)
Example 14	1.5	150	0.5	30.0	0	12.0	O	150	0.6	excellent	excellent	A/B/C/B/A (five layers)
Comparative Example 15	0.5	no chain-like silica		0.1	3.0	71.0	O	320	1.2	not good	not good	A/B/C/B/A (five layers)

Example 15 (Table 5)

Calcium carbonate particles having a mean primary particle size of 0.8  $\mu\text{m}$  prepared as particles B were dispersed in ethylene glycol using glass beads having a diameter of 50  $\mu\text{m}$  as medium. After removing the glass beads, the mixture was polymerized with terephthalic acid to make master pellets of polyethylene terephthalate.

On the other hand, alumina particles having a mean primary particle size of 10nm prepared as particles A, whose crystal form was  $\delta$ -type, were dispersed uniformly in ethylene glycol using the above media dispersion method, and master pellets containing particles A were prepared in a manner similar to that described above.

Chips (10 parts by weight) containing 10wt% dodecylbenzene sodium sulphate and 10wt% polyethylene glycol, the above master pellets containing particles B (20 parts by weight), the master fillets (30 parts by weight) containing particles A and pellets of polyethylene terephthalate with no particles were blended, and the blended pellets were supplied to a vent-type twin-screw extruder and melted at a temperature of 280°C (polymer I). Further, another extruder was prepared, the pellets with no particles were dried at a temperature of 180 °C for 8 hours (3 Torr), the dried pellets were supplied to the extruder and melted at a temperature of 290 °C (polymer II). After filtering these two polymers at a high accuracy in filtration degree, the polymers were laminated by a feed block for three layers having a rectangular shaped lamination portion so that the polymer II was positioned as the base layer and the polymer I was laminated on both surfaces of the base layer as both outermost layers. The laminated polymer was delivered out from a fish tail type die in the form of a sheet, the delivered sheet was cast on a casting drum of which surface temperature was controlled at 30°C and cooled and solidified on the drum using an electrostatic charging method to form a non-stretched film having a thickness of about 160 $\mu\text{m}$ . In this casting, the draft ratio was 6.5.

The non-stretched film obtained was stretched in the longitudinal direction at three stages the respective conditions of temperatures and draw ratios of which were 123 °C, 1.2 times; 126°C, 1.45 times; and 114 °C, 2.3 times. The uniaxially stretched film obtained was stretched, using a stenter, in the transverse direction at two stages the respective conditions of temperatures and draw ratios of which were 111°C, 3.7 times and 113 °C, 1.2 times, and heat treated at conditions of a temperature of 200 °C and a constant length for five seconds to make a biaxially oriented film having a thickness of 13  $\mu\text{m}$ . The relationship between the thickness T of the outermost layer and the particle size D of particles A was  $T=50D$ . The particle densities of particles A and the lamination thicknesses of both outermost layers were the same. The parameter of surface roughness P10 of this film was 85nm.

The electromagnetic conversion property of the film was 3.2dB in chromatic S/N. The abrasion resistance was 50 $\mu\text{m}$  and it was good. Thus, in a case where the kind, the particle size, the content, the particle density ratio at surface layer and the lamination thickness of the outermost layer satisfied the preferred ranges embodying the present invention a film having an excellent electromagnetic conversion property and a good abrasion resistance.

Examples 16 and 17, Comparative Examples 20 and 21 (Table 5)

Biaxially oriented laminated films were made in a manner similar to that of Example 15, and the particles were present in the outermost layers, dodecylbenzene sodium sulphate or dodecylbenzene lithium sulphate was also present and polyethylene glycol was present as polyalkylene glycol (Examples 16 and 17). Compared were the case where particles were not present and only dodecylbenzene sodium sulphate was present (Comparative Example 20) and the case where polyethylene glycol was present together with dodecylbenzene sodium sulphate but the content was out of the range according to the present invention (Comparative Example 21). It is understood that the surface resistivity is lowered by containing an appropriate amount of sulfonic acid metallic salt and polyethylene glycol and shaking of regenerated image can be prevented.

Comparative Examples 16-19 (Table 6)

Biaxially oriented laminated films were made in a manner similar to that of Example 15, changing the kind, the particle size, the content and the thickness T of the outermost layer. If any condition is out of the range required by the present invention, an excellent electromagnetic conversion property and a good abrasion resistance were not simultaneously achieved.

TABLE 5

	Particle in outermost layer				Parameter of surface roughness P10 (nm)	Electro-magnetic conversion property (dB)	Abrasion resistance ( $\mu\text{m}$ )	Composition contained in outermost layer	Surface resistivity ( $\Omega/\square$ )	Shaking of regenerated image
	Particle density ratio at surface layer	Content (wt%)	Particle size (nm)	T/D						
Example 15	0.04	0.3	10	50	85	+3.2	50	DEStNa 1% PEG 1%	$2 \times 10^{11}$	good
Example 16	0.10	0.3	10	60	100	+2.8	60	DEStNa 1.5% PEG 1%	$5 \times 10^{11}$	good
Example 17	0.08	0.2	5	80	95	+2.5	100	DESLi 1% PEG 0.5%	$5 \times 10^{11}$	good
Comparative Example 20	not contained	—	—	—	250	-0.1	—	DEStNa 1% —	$1 \times 10^{11}$	not good
Comparative Example 21	not contained	—	—	—	260	-0.1	—	DEStNa 0.1% PEG 0.1%	$2 \times 10^{11}$	not good

(Note) DEStNa : dodecylbenzene sodium sulphate

 $\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}$ 

DESLi : dodecylbenzene lithium sulphate

 $\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Li}$ 

PEG : polyethylene glycol

TABLE 6

	Particle in outermost layer				Recycle polymer in intermediate layer	Parameter of surface roughness P10 (nm)	Electro-magnetic conversion property (dB)	Abrasion resistance ( $\mu\text{m}$ )
	Particle density ratio at surface layer	Content (wt%)	Particle size (nm)	T/D				
Comparative Example 16	not contained	—	—	—	X	200	0	250
Comparative Example 17	not contained	—	—	—	X	300	-0.2	230
Comparative Example 18	0.005	2.5	500	5	X	250	+0.2	300
Comparative Example 19	0.002	0.5	500	0.8	X	220	+0.3	350

## Claims

1. A laminated film having at least three layers, at least one of which layers is biaxially oriented and an outermost layer A of which contains

a) inorganic particles A selected from zirconia, chain-like silica and alumina particles and having a mean primary particle size D which is in the range 1 to 100 nm and satisfies the equation

$$D \leq T \leq 200 D$$

where T is the thickness of the layer A; and

b) particles B selected from calcium carbonate particles, crosslinked polymer particles and colloidal silica particles and having a mean primary particle size D1 which is in the range 0.3 to 2  $\mu\text{m}$  and a primary particle size distribution with a relative standard deviation of not greater than 0.6; and, in which outermost layer A,

c) the mean primary particle size D of the particles A is less than the mean primary particle size D1 of the particles B.

2. A laminated film according to claim 1, wherein the inorganic particles A are distributed within the laminated film so that the ratio of the densities of particle distribution, each determined by SIMS along a direction of thickness of the film, at respective depths 3 nm and 30 nm at a surface layer A is not less than 0.01.

3. A laminated film according to claim 1, wherein the outermost layer A containing the particles A is composed of polyester.

4. A laminated film according to any preceding claim, wherein the content of the particles A in the outermost layer A containing the particles A is in the range of 0.01 to 2% by weight.

5. A laminated film according to any preceding claim, wherein the ratio of the mean secondary particle size to the mean primary particle size of the particles A is in the range of 2 to 60.

6. A laminated film according to any preceding claim, wherein the mean primary particle size D1 of the particles B and the thickness T of the outermost layer A containing the particles B satisfies the equation:

$$0.5D1 \leq T \leq 5D1.$$

7. A laminated film according to any preceding claim, wherein the content of the particles B in the layer containing the particles B is in the range of 0.005 to 5% by weight.

8. A laminated film according to any preceding claim, wherein the particles B are vaterite-type calcium carbonate particles.

9. A laminated film according to any preceding claim, wherein particles C having a mean primary particle size greater than that of the particles A and smaller than that of the particles B are also contained in the layer A containing the particles A and the particles B.

10. A laminated film according to any preceding claim, wherein the particles A are provided by non-incorporated particles which are seed particles.

11. A laminated film according to any preceding claim, which laminated film has at least four layers, namely an intermediate layer, cover layers laminated on both surfaces of the intermediate layer and the outermost layer containing the particles A laminated on at least one of the cover layers.

12. A laminated film according to claim 11, wherein the thickness of the intermediate layer is not less than 0.1  $\mu\text{m}$ .

13. A laminated film according to claim 11 or 12, wherein the thickness of each of the cover layers is not less than 0.2  $\mu\text{m}$ .

14. A laminated film according to any of claims 11 to 13, wherein the content of particles in each of the cover layers is not greater than 2% by weight.

15. A laminated film according to any preceding claim, wherein the surface resistivity of at least one outermost layer of the biaxially oriented laminated film is not greater than  $1 \times 10^{14} \Omega/\square$ .

16. A laminated film according to claim 15, wherein the said at least one outermost layer with a surface resistivity of not greater than  $1 \times 10^{14} \Omega/\square$  contains sulphate of 0.2 to 5% by weight.

#### Patentansprüche

1. Verbundfolie mit zumindest drei Schichten, wobei zumindest eine dieser Schichten biaxial orientiert ist und von denen eine äußerste Schicht A folgendes enthält:

a) anorganische Teilchen A, ausgewählt aus Teilchen aus Zirkonoxid, kettenartiger Kieselsäure und Aluminiumoxid, mit einer mittleren Primärteilchengröße D im Bereich von 1 bis 100 nm, die der Gleichung

$$D \leq T \leq 200 D$$

genügt, worin T die Dicke der Schicht A ist; und

b) Teilchen B, ausgewählt aus Teilchen aus Kalziumcarbonat, vernetztem Polymer und kolloidaler Kieselsäure, mit einer mittleren Primärteilchengröße D1 im Bereich von 0,3 bis 2  $\mu\text{m}$  und einer Primärteilchen-Größenverteilung mit einer relativen Standardabweichung von höchstens 0,6; und in welcher äußersten Schicht A

c) die mittlere Primärteilchengröße D der Teilchen A geringer als die mittlere Primärteilchengröße D1 der Teilchen B ist.

2. Verbundfolie nach Anspruch 1, worin die anorganischen Teilchen A solcherart in der Verbundfolie verteilt sind, daß das Verhältnis der Teilchenverteilungsdichten, die jeweils in Dickerichtung der Folie mittels SIMS bestimmt werden, in Tiefen von 3 bzw. 30 nm einer Oberflächenschicht A zumindest 0,01 beträgt.

3. Verbundfolie nach Anspruch 1, worin die die Teilchen A enthaltende, äußerste Schicht A aus Polyester besteht.

4. Verbundfolie nach einem der vorhergehenden Ansprüche, worin der Gehalt an Teilchen A in der die Teilchen A enthaltenden, äußersten Schicht A im Bereich von 0,01 bis 2 Gew.-% liegt.

5. Verbundfolie nach einem der vorhergehenden Ansprüche, worin das Verhältnis der mittleren Sekundärteilchengröße zur mittleren Primärteilchengröße der Teilchen A im Bereich von 2 bis 60 liegt.

6. Verbundfolie nach einem der vorhergehenden Ansprüche, worin die mittlere Primärteilchengröße D1 der Teilchen B und die Dicke T der die Teilchen B enthaltenden, äußersten Schicht A der folgenden Gleichung genügt:

$$0,5 D1 \leq T \leq 5 D1.$$

7. Verbundfolie nach einem der vorhergehenden Ansprüche, worin der Gehalt an Teilchen B in der die Teilchen B enthaltenden Schicht im Bereich von 0,005 bis 5 Gew.-% liegt.

8. Verbundfolie nach einem der vorhergehenden Ansprüche, worin die Teilchen B Kalziumcarbonatteilchen vom Vaterit-Typ sind.

9. Verbundfolie nach einem der vorhergehenden Ansprüche, worin auch Teilchen C mit einer mittleren Primärteilchengröße, die größer als jene der Teilchen A und kleiner als jene der Teilchen B ist, in der die Teilchen A und die Teilchen B enthaltenden Schicht A enthalten sind.

10. Verbundfolie nach einem der vorhergehenden Ansprüche, worin die Teilchen A durch nicht-eingearbeitete Teilchen, die Kristallkeime sind, bereitgestellt sind.

11. Verbundfolie nach einem der vorhergehenden Ansprüche, die zumindest vier Schichten aufweist, d.h. eine Zwischenschicht, auf beiden Oberflächen der Zwischenschicht auflaminierte Deckschichten, und die äußerste Schicht, die die Teilchen A enthält und auf zumindest auf einer der Deckschichten auflaminiert ist.

12. Verbundfolie nach Anspruch 11, worin die Dicke der Zwischenschicht nicht weniger als 0,1  $\mu\text{m}$  beträgt.



13. Verbundfolie nach Anspruch 11 oder 12, worin die Dicke jeder der Deckschichten nicht weniger als 0,2 µm beträgt.
14. Verbundfolie nach einem der Ansprüche 11 bis 13, worin der Teilgehalt in jeder der Deckschichten nicht mehr als 2 Gew.-% beträgt.
15. Verbundfolie nach einem der vorhergehenden Ansprüche, worin der Oberflächenwiderstand zumindest einer äußersten Schicht der biaxial orientierten Verbundfolie nicht mehr als  $1 \times 10^{14} \Omega/\square$  beträgt.
16. Verbundfolie nach Anspruch 15, worin die zumindest eine äußerste Schicht mit einem Oberflächenwiderstand von höchstens  $1 \times 10^{14} \Omega/\square$  0,2 bis 5 Gew.-% Sulfat enthält.

## Revendications

1. Film multicouche ayant au moins trois couches, au moins l'une desdites couches est biaxialement orientée et dont une couche externe A contient

a) des particules inorganiques A sélectionnées parmi des particules de zirconia, d'alumine et de silice en chaîne et ayant une grandeur moyenne primaire de particules D qui est comprise entre 1 et 100 nm et satisfait à l'équation

$$D \leq T \leq 200 D$$

où T est l'épaisseur de la couche A; et

b) des particules B sélectionnées parmi des particules de carbonate de calcium, des particules d'un polymère réticulé et des particules de silice colloïdale et ayant une grandeur moyenne primaire de particules D1 qui est de l'ordre de 0,3 à 2 µm et une distribution de grandeur des particules primaire avec un écart standard relatif de pas plus de 0,6; et dans ladite couche externe A,

c) la grandeur moyenne primaire des particules D des particules A est plus petite que la grandeur moyenne primaire D1 des particules B.

2. Film multicouche selon la revendication 1, où les particules inorganiques A sont distribuées dans le film multicouche de façon que le rapport des densités de la distribution des particules, chacune déterminée par SIMS le long d'une direction d'épaisseur du film, à des profondeurs respectives de 3 nm et 30 nm à une couche de surface A, ne soit pas de moins de 0,01.

3. Film multicouche selon la revendication 1, où la couche externe A contenant les particules A se compose de polyester.

4. Film multicouche selon toute revendication précédente, où la teneur en particules A dans la couche externe A contenant les particules A est de l'ordre de 0,01 à 2% en poids.

5. Film multicouche selon toute revendication précédente, où le rapport de la grandeur secondaire moyenne de particules à la grandeur moyenne primaire de particules des particules A est de l'ordre de 2 à 60.

6. Film multicouche selon toute revendication précédente, où la grandeur moyenne primaire de particules D1 des particules B et l'épaisseur T de la couche externe A contenant les particules B satisfait à l'équation :

$$0,5D1 \leq T \leq 5D1.$$

7. Film multicouche selon toute revendication précédente, où le contenu des particules B dans la couche contenant les particules B est de l'ordre de 0,005 à 5% en poids.

8. Film multicouche selon toute revendication précédente, où les particules B sont des particules de carbonate de calcium du type vatérite.

9. Film multicouche selon toute revendication précédente, où des particules C ayant une grandeur moyenne primaire de particules plus grande que celle des particules A et plus petite que celle des particules B sont également contenues dans la couche A contenant les particules A et les particules B.

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10. Film multicouche selon toute revendication précédente, où les particules A sont formées de particules non incorporées qui sont des particules d'ensemencement.
- 5 11. Film multicouche selon toute revendication précédente, lequel film multicouche a au moins quatre couches, c'est-à-dire une couche intermédiaire, des couches de recouvrement laminées sur les deux surfaces de la couche intermédiaire et la couche externe contenant les particules A laminée sur au moins l'une des couches de recouvrement.
- 10 12. Film multicouche selon la revendication 11, où l'épaisseur de la couche intermédiaire n'est pas de moins de 0,1  $\mu\text{m}$ .
13. Film multicouche selon la revendication 11 ou 12, où l'épaisseur de chacune des couches de recouvrement n'est pas de moins de 0,2  $\mu\text{m}$ .
- 15 14. Film multicouche selon l'une quelconque des revendications 11 à 13, où la teneur des particules dans chacune des couches de recouvrement ne dépasse pas 2% en poids.
15. Film multicouche selon toute revendication précédente, où la résistivité de surface d'au moins une couche externe du film multicouche biaxialement orienté n'est pas plus grande que  $1 \times 10^{14} \Omega/\square$ .
- 20 16. Film multicouche selon la revendication 15, où ladite au moins une couche externe avec une résistivité de surface de pas plus de  $1 \times 10^{14} \Omega/\square$  contient du sulfate à raison de 0,2 à 5% en poids.

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